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(54) Title: PURIFICATION OF 1,1,1,3,3-PENTAFLUOROPROPANE (R-245fa) (57) Abstract 1-Chloro-3,3,3-trifluoropropene (R-1233zd) or other olefin impurities are removed from 1,1,1,3,3-pentafluoropropane (R-245fa) by contacting the R-245fa in the liquid or vapor phase with chlorine in the presence of ultraviolet light providing an exposure of at least about 0.02 watts-hour/kg.		

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PURIFICATION OF 1,1,1,3,3-PENTAFLUOROPROPANE (R-245fa)

BACKGROUND OF THE INVENTION

This invention relates principally to the purification of 1,1,1,3,3-pentafluoropropane, also designated R-245fa, which has been of particular interest as a replacement for chlorofluorocarbons having similar physical properties, particularly R-113. R-245fa may be prepared by a three-step process involving reaction of chloroform, CCl_4 , with vinylidene chloride, $\text{CH}_2=\text{CCl}_2$, reacting the product with HF to form $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ (R-235fa) and finally, hydrogenation to remove the chlorine atom, as disclosed in pending U.S. Serial No. 08/099,676.

It is characteristic of such reactions that many by-products are formed, containing varying numbers of hydrogen, chlorine, and fluorine atoms on $\text{C}_1\text{-C}_3$ compounds. These by-products and the unreacted feed material may be separated by distillation where possible. Some compounds are relatively harmless since their presence does not greatly alter the physical properties for which R-245fa is useful. One by-product which must be removed because of its toxicity is 1-chloro-3,3,3-trifluoropropene (R-1233zd), although only relatively small amounts are typically present in R-245fa as formed. R-1233zd has a boiling point close to that of R-245fa making them difficult to separate by distillation. After distillation of the crude product, R-1233zd will still be present in amounts from about 300 to 20,000 ppm (wt.). It should be reduced to below 20 ppm according to the specifications of the Panel for Advancement of Fluorocarbon Test (PAFTII). Preferably, the R-1233zd should be below about 10 wt. ppm.

Further improvement in methods of purifying R-245fa, particularly with respect to eliminating R-1233zd is desired and the present inventors have discovered a means for purification by photochlorination which will be disclosed in detail below.

In addition to R-1233zd, there may be several other unsaturated by-products present which would be expected to be removed by a process which removes R-1233zd, for example, R-1223xd, R-1224zb, R-1224xe, R-1233xf, and the like

SUMMARY OF THE INVENTION

1-chloro-3,3,3-trifluoropropene (R-1233zd) is removed from a mixture consisting substantially of 1,1,1,3,3-pentafluoropropane (R-245fa) and containing up to about 20,000 wt. ppm R-1233zd by contacting the R-245fa mixture with 1-5 mols of chlorine for each mol of R-1233zd in the presence of ultraviolet light having a wave length between about 300 to 400 nm which provides at least 0.02 watts-hour/kg of the mixture, preferably 0.02 to 2.0 watts-hour/kg. The R-1233zd can be reduced to below 10 wt. ppm or lower, as it is converted to 1,2,2-trichloro-3,3,3-trifluoropropane (R-233) or other propanes containing more chlorine such as R-223 or R-213, which have higher boiling points and can be easily separated from R-245fa. Other unsaturated compounds, such as R-1233xd, R-1224zb, R-1224xe, and R-1233xf, are also removed by chlorination to other derivatives which can be separated, for example by distillation. The temperature and pressure used may be adjusted to provide R-245fa in either the vapor or liquid phase, the liquid phase being preferred.

The photochlorination of R-245fa may produce as a by-product 3-chloro-1,1,1,3,3-pentafluoropropane (R-235fa).

DETAILED DESCRIPTION OF THE INVENTION

R-245fa may be produced by the process of USSN 08/099,676, beginning from chloroform and vinylidene chloride. The crude product will contain a variety of byproducts. It is of particular importance to remove 1-chloro-3,3,3-trifluoropropene (R-1233zd) from the crude product. Preliminary separation of R-245fa by distillation will leave about 300 to 20,000 wt. ppm of R-1233zd having a boiling point of 19.2°C compared to 15.3°C for R-245fa, the difference in boiling points making R-1233zd difficult to separate from R-245fa. In the process of the invention, R-1233zd or other unsaturated compounds which may be present, e.g. R-1233xd, R-1224zb, R-1224xe, R-1233xf, are reacted with chlorine to provide more highly chlorinated compounds which have a higher boiling point and can be readily

separated from R-245fa. Optionally, R-235fa may be co-produced by chlorination of R-245fa.

Process Conditions

5 In the process, crude R-245fa containing about 300 to 20,000 wt. ppm of R-1233zd along with minor amounts of other byproducts such as those mentioned above will be contacted with chlorine in the presence of ultraviolet light having a wavelength of about 300 to 400 nm. It should be understood that an ultraviolet lamp may have radiation outside this range also, but that photochlorination requires UV
10 light within this range.

The ultraviolet light will have an intensity which provides an exposure greater than zero and at least about 0.02 watts-hour/kg of the R-245fa mixture, preferably 0.02 to 2.0 watts-hour/kg.

15 The ultraviolet light may be provided by arc lamps including mercury, argon, or xenon and filament lamps including tungsten and halogen.

Chlorine is introduced into the crude R-245fa stream at a rate sufficient to provide about 1 to 5 mols of chlorine for each mol of R-1233zd, preferably 1 to 1.5.

20 It has been found that increasing either the ratio of chlorine to R-1233zd ($\text{Cl}_2/\text{R-1233zd}$) or the ultraviolet light exposure improves the chlorination of R-1233zd. Generally, we have been able to reduce the R-1233zd to below 10 wt. ppm using a UV exposure above about 0.04 watts-hour/kg but with quite low ratios of $\text{Cl}_2/\text{R-1233zd}$. Conversely, much lower UV exposures can be used if higher $\text{Cl}_2/\text{R-1233zd}$ ratios are used. The $\text{Cl}_2/\text{R-1233zd}$ ratio and UV exposure may be adjusted to provide the desired set of conditions.

25 The temperature employed may vary but may be from about -50°C to 200°C , preferably about 25° to 60°C .

The pressure selected will be a convenient value to suit the processing conditions for R-245fa and to assure that R-245fa is a liquid or vapor, as desired.

The UV radiation from a lamp ordinarily will be expressed as watts, which is a rate of delivering energy. For present purposes, it is considered more useful to express radiation as the quantity of energy delivered over a period of time, i.e. the "exposure," rather than as the rate. Thus, the exposure may be expressed as watts-
5 hours, which is related to the number of photons of energy delivered and their wavelength and these, in turn, relate to the chlorination of unsaturated molecules such as R-1233zd. Since the exposure is the product of the rate of delivering energy (photons/time) and the time, it will be clear that either the rate or the time could be varied. However, for practical applications the rate and the time will have limits
10 imposed by the need to carry out the desired photochlorination reaction within constraints of time and product yield. If a high rate or a long time is used, not only will R-1233zd be chlorinated to R-233 (or R-223 or R-213), but chlorine will react with other molecules, particularly with R-245fa to make R-235fa. Alternatively, if a very low rate or a short time is used, then insufficient chlorination of R-1233zd would
15 be expected.

When co-production of 3-chloro-1,1,1,3,3-pentafluoropropane (R-235fa) is desired, the ratio of chlorine to R-245fa can be increased. Preferably, the U.V. exposure will be about 1.5 to 5.0 watts-hour/kg of R-245fa and the $\text{Cl}_2/\text{R-1233zd}$ ratio (mol) about 1-50 to 1. It will be understood by those skilled in the art
20 that the operating conditions may be adjusted to optimize the relative amounts of R-235fa and R-245fa.

After the R-245fa has been photochlorinated, the chlorinated products may be separated from the R-245fa, as, for example, by distillation, since the boiling points are no longer close to that of R-245fa. Any residual chlorine, HCl or HF may
25 be separated by absorption of chlorine in aqueous caustic, by adsorption on carbon molecular sieves, or reaction with aqueous sodium sulfite or sodium thiosulfate.

Example 1Liquid phase purification of R-245fa

The photochlorination of R-245fa was carried out in a 125 mL pyrex pressure vessel equipped with a dip leg inlet and a pressure gauge. This vessel was chilled in ice water and 20.0 grams of impure G-245fa, containing 0.08% R-1233zd was condensed into it. Then, while still cold, a stream of chlorine gas was passed at 10 mL/min through this solution for exactly 52 seconds. We calculate according to the ideal gas law that this should correspond to 3.6×10^{-4} moles of chlorine, or a 1:1 mole ratio with the R-1233zd impurity. The vessel was then allowed to warm to room temperature.

The reactor vessel was placed for 5 minutes at the focus of RPR-100 Rayonet reactor (Southern New England Ultraviolet Company) equipped with 16 RPR-3500 lamps having their peak intensity at a wavelength of 350 nm. Light below 300 nm was removed by the pyrex walls of the pressure vessel. Ferrioxalate actinometry was used to measure the radiation received (see The Chemists Companion, A. J. Gordon & R. A. Ford, Wiley Interscience (1972), pages 362-368). In this vessel under these conditions this procedure gave an incident light intensity of 1.317×10^{-7} einstein/sec (0.0417 watts). (One einstein is an equal to a mol of photons.) A five minute exposure should therefore have supplied 3.95×10^{-5} einsteins of light (0.039 watt-hour/kg).

After exposure, the vapor head of the pressure vessel was sampled by gas chromatography using a 3048 mm long x 3.175 mm diameter column of 1% SP1000 on 60-80 mesh Carbopack B (Supelco Inc.) packing operated at 45°C for 3 minutes and then programmed to increase 8°C/min to 200°C. This stream contained 0.00335 % R-1233zd, and 0.0793 % R-235fa.

Example 2Vapor phase purification of R-245fa

The photochlorination of R-245fa was carried out in a 125-mL pyrex pressure vessel equipped with an inlet at the bottom and an outlet at the top. The reactor vessel was placed at the focus of RPR-100 Rayonet reactor (Southern New

England Ultraviolet Company) equipped with 16 RPR-3500 lamps having their peak intensity at a wavelength of 350 nm. Light below 300 nm was removed by the pyrex walls of the vessel. The vessel was immersed in a pyrex constant temperature bath held at 59 °C to ensure that the G-245fa remained in the vapor phase.

Two feed streams were passed through separate lengths of capillary tubing and then mixed and passed into the reactor at 5 psig (34.5 kPa gauge). The impure R-245fa contained 0.080 % R-1233zd plus other impurities. One stream contained impure R-245fa while the second contained chlorine. By blending the two streams the ratio of chlorine to R-1233zd was varied. The radiation exposure was calculated from the residence time and the light intensity and varied from 2 to 3.5 watts-hour/kg. After exposure to the ultraviolet light the product stream was analyzed by gas chromatography using the procedures of Example 1.

The results of the tests at lower ratios of Cl₂/R-1233zd are given in Table 1. The compounds are designated as refrigerants (R) according to the commonly used system of the American Society of Refrigerating Engineers.

Table 1
Vapor Phase Photochlorination to Remove Olefinic Impurities

R-245fa Flow Rate (mL/min)	Chlorine Flow Rate (mL/min)	Estimated Chlorine/G-1233zd Molar Ratio	Conc. R-1233zd (%)	Conc. R-235fa (%)
Feed	—	—	0.0800	0.00091
49	3.0	26.5	0.0080*	1.232
49	5.7	48.0	N.D.	8.789
91	0.99	4.7	0.00319	2.554

* value suspect, R-1233zd concentration should have been low since R-235fa has been produced.

Example 3Effect of Chlorine Ratio on R-245fa Purity

A series of experiments were done using the same general procedure as that described in Example 1. However, for each experiment, the weight of G-245fa, and the amount of chlorine introduced was changed, so as to explore the effect of changing the ratio of these reactants. All samples were exposed to UV light as described in Example 1 for 1 minute. Then GC analysis was completed as described. The amounts of reagents and experimental results are shown in Table 2 below.

Table 2Effect of Chlorine Ratio on Performance in Liquid Phase

Weight G-245fa (g)	Chlorine Flow rate (mL/min)	Chlorine Flow time (sec)	Calculated Moles Chlorine ($\times 10^5$)	Calculated $\text{Cl}_2/\text{R-1233zd}$ Molar Ratio	Conc. of R-1233zd (%)	Conc. of R-235fa (%)
Feed	—	—	—	—	1.04	0.0027
17.3	2.97	30	5.8	0.096	0.935	N.D.
21.5	10.33	30	20.3	0.27	0.54	0.01
9.5	10.32	24	16.2	0.495	0.40	0.191
8.20	10.34	32	21.6	0.76	0.017	1.85
11.8	10.34	60	40.6	1.00*	0.829*	N.D.*
23.7	10.33	160	108.1	1.22	0.0003	0.66
23.9	10.33	180	121.6	1.47	N.D.	4.05

*Air contamination suspected, which will prevent the photochlorination from occurring.

It can be seen that the concentration of R-1233zd decreases as the ratio of $\text{Cl}_2/\text{R-1233zd}$ is increased. Theoretically one mol of chlorine can react with one mol of R-1233zd to yield one mol of R-233. The results show that at a ratio of about

1.47/1 essentially all of the R-1233zd has been converted within the limits of analytical precision. The product of chlorination of R-245fa, i.e., R-235fa is seen to appear at a ratio of about 0.5/1. Therefore, the preferred ratio of $\text{Cl}_2/\text{R-1233zd}$ is considered to be about 1.0/1 to 1.3/1 when only the removal of R-1233zd is desired.

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Example 4

Effect of Light Intensity on Photochlorination Performance

A series of experiments were done using the same general procedure as that described in Example 1. However, for each experiment, the light intensity was varied by varying the number of light bulbs used in the Rayonet reactor. Ferrioxalate actinometry was used to measure the radiation received (see The Chemists Companion, A. J. Gordon & R. A. Ford, Wiley Interscience (1972), pages 362-368). All samples were exposed to UV light as described in Example 1 for 1 minute. Then GC analysis was completed as described. The amounts of reagents and experimental results are shown in Table 3 below.

15

Table 3

Effect of Light Intensity on Performance in Liquid Phase

Weight G-245fa (g)	Chlorine Flow rate (mL/min)	Chlorine Flow time (sec)	Calculated Moles Chlorine ($\times 10^5$)	Calculated $\text{Cl}_2/\text{R-1233zd}$ Molar Ratio	Light Intensity (Einsteins/ $\text{sec} \times 10^3$)	Conc. of R- 1233zd (%)	Conc. of R-235fa (%)
Feed	—	—	—	—	—	1.04	0.0027
23.1	10.32	118	79.7	1.0	1.317	0.00574	3.02
19.3	10.32	99	66.6	1.0	1.181	0.0764*	0.799*
15.5	10.32	79	55.4	1.0	0.866	0.0112	2.678
14.8	51.1	76	51.1	1.0	0.410	0.1116	2.047

*Air contamination suspected

This set of experiments shows that, as might be expected for a light-driven reaction, more light results in higher conversions. This effect is evident both in the conversion of R-1233zd to more highly chlorinated species and the conversion of

20

R-245fa to R-235fa. The experimental results can also be used to measure the quantum yield of the process, which is defined as the ratio of the rate of chlorination (in moles/second) and the intensity of light incident on the sample (in einsteins/second). Since an einstein is a mole of photons, this quantity is unitless. We
5 calculate that the quantum yield measured in this set of experiments is roughly 100.

CLAIMS:

1. A process for removing 1-chloro-3,3,3-trifluoropropene (R-1233zd) or other olefinic impurities from 1,1,1,3,3-pentafluoropropane (R-245fa) comprising
 - (a) contacting a mixture consisting substantially of R-245fa and up to about 20,000 wt. ppm R-1233zd with about 1-5 mols of chlorine for each mol of R-1233zd or other olefins in the presence of ultraviolet light having wavelengths between about 300 and 400 nm providing an exposure greater than zero and at least 0.02 watts-hour/kg of said mixture, thereby reducing the concentration of R-1233zd or other olefins to less than 10 wt. ppm by converting said R-1233zd to 1,2,2-trichloro-3,3,3-trifluoropropane (R-233) or propanes containing greater amounts of chlorine; and
 - (b) separating the R-233 formed in (a) from R-245fa.
2. The process of Claim 1 wherein said R-245fa is chlorinated in part to co-produce 3-chloro-1,1,1,3,3-pentafluoropropane (R-235fa).
3. The process of Claim 1 wherein said ultraviolet light provides an exposure of about 0.02 to 2 watts-hour/kg of said mixture.
4. The process of Claim 1 wherein about 1 to 1.5 mols of chlorine are present for each mol of R-1233zd.
5. The process of Claim 1 wherein the contacting of (a) is carried out at a temperature and a pressure sufficient to assure that R-245fa is liquid.
6. The process of Claim 1 wherein the contacting of (a) is carried out at a temperature and a pressure at which R-245fa is vapor.
7. The process of Claim 1 wherein the temperature is in the range of about -50°C to 200°C.
8. The process of Claim 7 wherein the temperature is in the range of about 25°C to 60°C.

9. The process of Claim 1 wherein the separation of (b) is carried out by distillation.

10. The process of Claim 1 wherein said other olefinic impurities comprise at least one member of the group consisting of R-1223xd, R-1224zb, R-1224xe, and
5 R-1233xf.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/395 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 12058 A (ALLIED SIGNAL INC) 24 June 1993 see claims	1
A	US 4 948 479 A (BROOKS WAYNE E ET AL) 14 August 1990 see claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Authorized officer

Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
W0 9312058 A	24-06-93	US 5336377 A	09-08-94
		AU 3243593 A	19-07-93
		BR 9206948 A	28-11-95
		CA 2125775 A	24-06-93
		CN 1074207 A	14-07-93
		EP 0618888 A	12-10-94
		JP 2547519 B	23-10-96
		JP 6510797 T	01-12-94

US 4948479 A	14-08-90	AT 113023 T	15-11-94
		CA 2014945 A,C	07-12-90
		DE 69013401 D	24-11-94
		EP 0401493 A	12-12-90
		ES 2062154 T	16-12-94
		JP 3024024 A	01-02-91
		JP 7091203 B	04-10-95
